SYNOPSIS

1. TITLE OF THE THESIS

KINETIC STUDY OF ADSORPTION OF SOME TOXIC METAL IONS BY USING IRON DOPPED ADSORBENTS

2. INTRODUCTION

Water pollution is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards [1]. Environmental problems have become more frequent and complex in recent decades, as a result of human population growth and increasing industrialization. Heavy metals are the main hazardous, non-degradable substances, persistence and can accumulate in the environment such as food chain, thus may pose a significant danger to human health [2]. Studies on the treatment of effluents containing heavy metal have revealed adsorption to be a highly effective technique for the removal of toxic metals from wastewater. Adsorption has been found to be superior to other techniques for water reuse in terms of the initial cost, simplicity of design and easiness of operation [3]. Adsorption is a universal and alternative technique for removal of organic and inorganic pollutants from waste water [4].

For the present work, the base material will be selected as Modified Polymer (Calcium Alginate) / Fruit peels (Orange Peel, Pomegranate Peel) / Saw Dust / Fly ash. Biopolymers (calcium alginate) are non-toxic, selective, efficient and inexpensive and thus highly competitive with ion-exchange resins and activated carbon. Alginates present in algae are capable of binding heavy metals through their carboxyl groups [5]. Fruits and their products can serve as a vehicle for wastewater treatment. The use of fruits peel not only provide a less costly adsorbent in contrast to activated carbon or synthetic ion exchangers but it is also easily available and will save the environment from the pollution due to the easy availability, low cost, simple preparation manner of adsorbents and effective adsorption capacity. The carboxyl and hydroxyl groups in these adsorbents are believed to react with heavy metal ions in aqueous solution [6].

Saw dust are inexpensive, abundant and contain polyphenolic groups that are capable of adsorbing significant quantities of metal cations from solution [7]. Fly ash has potential applications in wastewater treatment because of its chemical composition, low cost

and good adsorbent properties like porosity, large surface area and particle size distribution [8].

3. A BRIEF REVIEW OF THE WORK ALREADY DONE IN THE FIEILD

Vijaya et al [7] studied column flow techniques for removal of nickel (II) from aqueous solutions through adsorption on to biopolymer sorbents synthesized like calcium alginate (CA), chitosan coated calcium alginate (CCCA) and chitosan coated silica (CCS). The maximum monolayer adsorption capacity of CA, CCCA and CCS was 310.4, 222.2 and 254.3mg/g for Ni(II), respectively. Biosorption of Ni(II) ion followed the pseudo-second order kinetics. P. S. Harikumar et al [9] synthesized entrapped iron nanoparticle (Fe_2O_3) in biopolymer (Ca-alginate beads) and removed arsenic (As) and they observed that entrapped iron nanoparticle (Fe_2O_3) in biopolymer showed better adsorption than bare Ca-alginate beads in adsorption process. They got 99.9% removal of arsenic in aqueous solution. Sergios K. Papageorgiou et al [3] have observed binary adsorption of Cu^{2+}-Cd^{2+}, Pb^{2+}-Cd^{2+} and Pb^{2+}-Cu^{2+} mixtures onto Ca-alginate beads, prepared from laminaria digitata, was studied using batch experiments. Langmuir isotherm accurately predicted the experimental results for all the metal mixtures. Torrres et al [10] et al reported gold (Au) and silver (Ag) adsorbed in calcium alginate beads. They determined that both carboxylic and hydroxyl functional group in alginate beads are involved in the metal binding and later reduction of gold (+3) and silver (+1) to gold (0) and silver (0). Ashtoukhy et al [11] et al used pomegranate peel as a new adsorbent. They prepared activated carbon from pomegranate peel and chemically treated pomegranate peel. They used phosphoric acid and zinc chloride for treated pomegranate peel. They reported order to fit the isotherms: Langmuir>Temkin>Freundlich for lead ions, Freundlich >Temkin >Langmuir for copper ions. Nevine Kamal Amin [12] synthesized activated carbon from pomegranate peel for removal of dye from waste water. Adsorption kinetics follow pseudo-second-order rate kinetic model, and intra-particle diffusion was one of the rate determining steps. Langmuir, Freundlich, Temkin, Dubinin–RadushKevich (D–R) and Harkins–Jura isotherms were used to analyze the equilibrium data at different temperatures. They observed thermodynamic parameters indicate the spontaneous and exothermic nature of the adsorption process. Bozic et al [13] reported particle size of the sawdust does not affect the process. The following series was obtained: Cu^{2+}>Zn^{2+}>Ni^{2+} >Cd^{2+}>Mn^{2+}>$Fe^{2+.}$ The adsorption kinetics was so fast and after 10–20 min of contact time, the system was closed to equilibrium. The kinetics considered as pseudo-second order reaction.

Marina Sciban et al [14] measured modification effect on saw dust by using formaldehyde and sodium hydroxide. They reported adsorption of Zn^{2+} and Cu^{2+} ions from formaldehyde and sodium hydroxide treated saw dust. They showed higher adsorption capacity than modification only with formaldehyde treated saw dust or sodium hydroxide treated saw dust. Modified saw dust shows 99% removal of Zn^{2+} and Cu^{2+} ions. Munusamy Thirumavalavan et al [15] have reported effective adsorbents like orange peel (OP), lemon peel (LP), and banana peel (BP) LPCACS (lemon peel cellulose acid carboxylation after safonification), AC (activated carbon) LPC (lemon peel cellulose) for removal of heavy metal ions such as Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} from aqueous solution. Order of the adsorption capacity was as follows: LPCACS >LPC > AC > LP > OP > BP. LPCACS was chemically modified by saponification and oxalic acid treatment method, after modification carboxylic group were increased rapidly. FENG Ning-chuan et al [16,17] prepared modified orange peel with sodium hydroxide and calcium chloride for sorption behavior of Cu^{2+}, $Pb^{2+}$and Zn^{2+} ions. Langmuir equation with the maximum adsorption capacities for Cu^{2+}, $Pb^{2+}$and Zn^{2+} of 70.73, 209.8 and 56.18 mg/g, respectively. Another work of those other shows adsorption of Cu^{2+} by chemically modified orange peels. Adsorption capacity of Cu^{2+} was 72.73 mg/g, chemically modified orange peels increase the number of carboxylate ligands, which would enhance the binding ability of the biomass. Xiaomin Li et al [18] studied chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co(II), Ni(II), Zn(II) and Cd(II). They reported effects of different chemical modifications on the adsorbent properties including different alkalis saponification (NaOH, NH_4OH and $Ca(OH)_2$) and different acids ($C_6H_6O_7 \cdot H_2O$, $H_2C_2O_4$ and H_3PO_4) modification after saponification with NaOH were investigated. Larous et al [19] used saw dust as an adsorbent for removal of Cu^{2+} ions from aqueous solution. A. M. Deshkar et al [20] used formaldehyde treated in acidic medium binta bark for sorption of Hg(II). They studied effect of metal cations on sorption of Hg(II). E. Klimiuk [21] et al studied effect of poly (vinyl alcohol) on adsorption of cadmium by using alginate adsorbents. Tingyi Liu et al [22] studied nanoscale zero-valent iron (NZVI) successfully entrapped in chitosan (CS) beads for reduction of Cr(VI) from wastewater. Nanoscale zero-valent iron (NZVI) inhenced the adsorption capacity of of beads. Ani Idris et al [23] reported reduction of Cr(VI) to Cr(III) in an aqueous solution under sunlight by using magnetic separable photocatalyst beads containing magnetic nanoparticles (Fe_2O_3) in polyvinyl alcohol (PVA). Wan Nag et al [24] have studied adsorption of Cu (II) ions onto

chitosan and cross-linked chitosan beads have been investigated. Chitosan beads were cross-linked with glutaraldehyde (GLA), epichlorohydrin (ECH) and ethylene glycol diglycidyl ether (EGDE). Uptake capacity of cross linked chitosan(80.71%), GLA-59.67%, ECH-62.475%, EGDE-45.94% mg/g. Tanja Becker et al [25] prepared cross-linked with a dialdehyde or a tetracarboxylic acid in order to obtain sorbents for removal of nickel(II), zinc(II) and cadmium(II). They have reported six types of derivatives which show good adsorption capacity. Ningchuan Fenga et al [26] prepared chemically modified orange peel as an adsorbent which was synthesized by interaction of methyl acrylate with cross-linking orange peel. Langmuir isotherm, the adsorption capacity for Cu(II) was 289.0mgg^{-1}. Salvatore Cataldo et al [27] reported Mercury(II) removal from aqueous solution by sorption onto alginate, pectate and polygalacturonate calcium gel beads. Langmuir and Freundlich isotherm equations show the following sorption capacity trend: Ca–Pect > Ca–PGA > Ca–A. Grigorios Itskos et al [28] have reported comparative sorption capacity of toxic elements from aqueous media by the different particle-size-fractions of fly ash of highly calcareous and highly siliceous fly ashes (FAs). Three different Hellenic FAs (two calcareous and one siliceous) were tested for capability of precipitating heavy metals from aqueous solutions. Highly calcareous fly ashes (KFA and PFA) showed efficient in uptake of Ni, Cu, Pb, Cd and Zn than highly siliceous fly ashes (MFA). The more Ca-rich of their particle-fractions (fine particles) presented the highest removal-efficiency. Vinay Kumar Jha et al [29] reported sorption properties of the activated carbon-zeolite composite prepared from coal fly ash for sorption of Ni^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+}. The equilibrium sorption capacity follows the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$.

4. OBJECTIVE OF RESEARCH

The main objectives of the present studies are:-

1. To study kinetics of adsorption of some toxic metals like Fe, Cr, Cd, Cu, Pb, Zn, Hg, Ni using chemically modified adsorbents.
2. To develop the adsorbents from wastes materials and polymeric nanomaterial for sorption/removal of heavy metals ions from aquatic medium.
3. To study the effect of initial metal concentration, pH, temperature, amount of adsorbent and time on the equilibrium.

4. Correlate the experimental data with the Langmuir and Freundlich isotherm models and other models also.
5. Investigate various thermodynamic parameters such as activation energy (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and Gibbs free energy of activation ($\Delta G^{\#}$).
6. To study of application of prepared adsorbents for removal of pollutants from water and waste water and analytical determination of their efficiency.

5. NOTEWORTHY CONTRIBUTION IN THE FIELD OF PROPOSED WORK

Audrey-Flore Ngomsik et al [30] synthesized a new magnetic alginate beads containing Cyanex 272 bis (2,4,4-trimethylpentyl) phosphinic acid for removing of Co(II) ions from aqueous solutions. Magnetic alginate beads containing Cyanex 272 good adsorption capacity. It contains active sites of the beads the presence of the phosphinic functions of Cyanex 272 and the carboxylate on the magnetic nanoparticles and alginate. V. Lugo-Lugo et al [31] presented biosorption of Cr(III) and Fe(III) in single and binary systems onto formaldehyde treated orange peel. The kinetic results showed a rapid rate of biosorption in single Cr(III) and Fe(III) systems and mutual interference effects in the competitive Cr(III), Fe(III) system. The adsorption of both metals in single and binary systems fits a pseudo-second order kinetic model. Carboxylic acid and hydroxyl group was the active sites of the adsorbent. Adsorbents contain functional groups like carboxyl, hydroxyl, amine and amide resulting in enhanced external surface area for metal ion adsorption. These works show that chemical modification of adsorbents convert in more effective than non-modified adsorbents. Chemical modification of polymer and other low cost adsorbents are improved the adsorption capacity of adsorbents due to higher number of active binding sites. It is helpful to synthesize low-cost, effective, easy separable adsorbents. Effective adsorbents offer a lot of promising benefits for commercial purpose in the future.

6. PROPOSED METHODOLOGY

Preparation of Adsorbents

Adsorbents for the adsorption of toxic metal ions, polymer entrapped nanoparticles will be used. Nanoparticles will be prepared in laboratory and entrapped in polymeric beads. Some metal nanoparticles will be used as adsorbent such as Ag and Fe etc. Beads will be used as an

adsorbent prepared in laboratory by using required chemicals like calcium alginate used as an entrapped material. Porosity in beads allows solute to diffuse onto the beads and come in contact with the entrapped material. To prepare adsorbent by waste material first of all, waste material will be dried and pulverize than after separated mean size particle by filtration. After washing and vacuum drying stock adsorbent will be obtained.

Reaction Conditions and Kinetic studies

pH: – pH is one of the most important parameters for the adsorption of heavy metal ions from aqueous solution. The pH of the solution is effect of surface charge on the adsorbent and the degree of ionization. The initial pH of the metal solution will be adjusted with required amount of acid / base. To study the effect of pH on sorption, the pH of the metal solution will be adjusted. Samples (required amount of adsorbent) are equilibrated with required amount of aqueous solution of metal ions at varying pH values.

Temperature: - Temperature is second most important parameters which play important role in adsorption of heavy metal ions. Temperature will be maintained (10-60˚C) by thermostatic water bath.

Time: - Kinetic experiments will be carried out by shaking the adsorption mixture at various predetermined intervals and analyzing the metal ion content at the end of the contact time. Pseudo first order equation, Pseudo-second-order equation, Elovich, Intra-particle diffusion equations will be used for kinetic studies.

Batch adsorption experiment

The isotherm curves and equilibrium sorption capacities will be determined in batch experiments at prefixed times in sealed conical flasks. Adsorption isotherms will be carried out with different initial metal concentrations of adsorbate varying and while holding the adsorbent required amount at fixed pH and temperature in a mechanical shake. After attending equilibrium, the adsorbent will be separated by filtration and the aqueous metal ion concentration will be identified by spectrophotometric method. Equilibrium sorption capacities for the each sample will be calculated according to batch equation. Langmuir, Freundlich, Temkin, Dubinin–RadushKevich (D–R) and Harkins–Jura models will be used for describe the adsorption equilibrium process.

Characterization:-

UV-Visible Spectrophotometeric and Atomic Absorption Spectrophotometeric Analysis- Metal ion concentration will be determined by UV-visible spectrophotometry and atomic absorption spectrophotometry.

FTIR (Fourier Transform Infrared Spectrophotometery):- FTIR is the powerful tool for identifying types of chemical bonds (functional groups). It is used to make sure the presence of capping agents. FTIR will be used to identify the chemical group present in the adsorbent.

SEM (Scanning Electron Microscopy):- Scanning electron microscope will be used for examine the morphology and surface structure of the adsorbents.

XRD (X-Ray Diffraction):- X-Ray diffraction study will be helpful to evaluate crystal quality and structural feature of the sample.

TEM (Transmissions Electron Microscopy):- TEM is the primary technique to determine crystal structure, crystalline shape and orientation of nanocrystals.

7. EXPECTED OUTCOME OF THE PROPOSED WORK:-

Adsorption technique is a highly effective technique for removal of toxic metal ions from waste water. In this study various adsorbents will be selected which play important role in adsorption of different toxic metal ions. Some novel adsorbents prepared by chemical modification will be selected. The proposed work will try to make chemically modified novel adsorbents for high sorption capacity, low cost, easily separable from aqueous solution, recyclable. All adsorbents have specific functional groups responsible for metal ions binding. Chemical modification of adsorbent will increase surface area and functional groups present on the surface of adsorbents. These properties will give significant influence on the performance of the adsorbents. The developed method can be successfully applied for removal of toxic metals from polluted water.

8. BIBLIOGRAPHY

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9. LIST OF PAPERS COMMUNICATED / SUBMITTED / PUBLISHED / IN JOURNALS / CONFERENCES / SYMPOSIUM

PAPER COMMUNICATED

1. "Synthesis of silver nanoparticles entrapped Ca-alginate beads for adsorption isotherm and kinetic studies for removal of Fe (II) ions from waste water"

PAPER PRESENTED IN CONFERENCES

1. "Adsorption of Fe (II) ions by using silver nanoparticles entrapped Ca-alginate beads for kinetic and thermodynamic studies"
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